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(54) Title: NONIONIC SOIL RELEASE AGENTS (57) Abstract Nonionic soil release agents having both oxyethylene and oxyiso-propyleneoxy units are useful in laundry compositions, especially in liquid through-the-rinse fabric softeners, as well as in detergent compositions. Thus, the reaction product of $\text{CH}_3(\text{OCH}_2\text{CH}_2)_{16}\text{OH}$, dimethyl terephthalate, polyethylene glycol 1500, 1,2-propylene glycol and ethylene glycol, preferably as a polymer/oligomer in which the ratio of incorporated ethylene glycol:propylene glycol is about 1.5:1, is added to a liquid fabric softener with DTDMAC. Fabrics rinsed in a bath containing this composition are both softened and afforded a soil release finish.		

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NONIONIC SOIL RELEASE AGENTS

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TECHNICAL FIELD

This invention relates to nonionic oligomers which function as improved soil release agents (sra's), and which are useful in laundry compositions, especially fabric softener compositions, and the like.

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BACKGROUND OF THE INVENTION

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A "soil release" effect is produced when fabrics, especially fabrics having a synthetic fiber component, are immersed in an aqueous laundry or rinse bath in a domestic or institutional setting wherein the aqueous bath comprises various polymeric or oligomeric ester soil release agents (sra's), typically at low levels such as five to a few tens of parts per million. The polymers or oligomers deposit onto the fabric surface to provide a soil-release finish thereto. Soil release is distinct from the usual cleaning effect of laundry detergent surfactants and builders, in that a multi-wash effect is secured, e.g., fabrics repetitively laundered tend to be cleaned progressively more easily over two, three or four wash-wear cycles, and some soil antiredeposition benefit is also often secured. Soil release is especially pronounced on polyester fabrics, but good results are also secured on polyester/cotton blends. Soil release benefits are also seen on nylons and acrylics.

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Soil release in an aqueous laundry context is rather different from industrial finishing of yarns and fibers, warp-sizing and the like, in terms of the general kinds of sra compositions which work best. This may be a consequence of some substantial differences in processing conditions. In any event, laundry sra's of the type herein are typically applied to fabrics in washing machines, either in the presence of noninterfering deterative surfactants, or, more preferably, in the presence of cationic fabric softening agents. The sra typically deposits to only a limited extent on the fabrics. In contrast, industrial finishing is commonly done in highly controllable process equipment, such as padders.

Typically the textile is clean, and the concentration of cleaning agents or softening agents (if any) tends to be low, at

least at the stage at which it is desired to exhaust a soil release treatment onto the textile substrate.

5 Just as there are technical differences between laundering and industrial finishing, so too are there considerable differences between laundry composition types, such as laundry detergents, laundry softeners, laundry bleaches, and the like. Such laundry compositions are also prepared in various forms, such as granular, liquid, gel, paste-form, and dryer-added products. Formulators in the laundry arts are acutely aware that various
10 forms of laundry compositions have inherent formulation constraints. For example, solid-formulated compositions need ingredients generally capable of dispersing or dissolving in aqueous laundry baths, while liquid formulae commonly need ingredients which are freely mixable without excessive chemical or physical
15 interaction such as phase changes or precipitation.

In particular, modern laundry compositions are now becoming available in popular "concentrate" form. For example, liquid fabric softeners have now been commercialized which contain cationic softener ingredients at concentrations on the order of
20 3-fold higher than fabric softeners available heretofore. It will be appreciated that the formulation of such compositions in shelf-stable form and at reasonable viscosity ranges can be difficult. Formulation and performance difficulties are, of course, accentuated when attempts are made to incorporate additional functional ingredients, such as sra's, into such
25 compositions.

Accordingly, there is a continuing search for effective, compatible, easy-to-formulate sra's for use in laundry compositions.

30 The present invention provides effective nonionic sra's which are suitable for use in laundry compositions. The invention also provides nonionic sra's which are particularly useful in combination with cationic fabric softeners. Moreover, many of the sra's herein do not excessively increase the viscosity of liquid fabric
35 softener compositions, even when formulated as softener "concentrates".

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BACKGROUND ART

U.S. Patent 4,711,730 to Gosselink and Diehl, December 8, 1987, relates to capped 1,2-propylene terephthalate - polyoxy-ethylene terephthalate polyesters useful as soil release agents in laundry detergents and fabric softener compositions, including concentrates.

Additional references in the field, as cited in Gosselink and Diehl, include the following.

A. Ethylene terephthalate/PEG terephthalate soil release polyesters used in laundry detergent compositions

U.S. Patent 4,116,885 to Derstadt et al, issued September 26, 1978, discloses laundry detergent compositions containing 0.15% to 25% (most preferably 0.5% to 10%) of an ethylene terephthalate/PEG terephthalate soil release polyester, such as MILEASE T, having an average molecular weight of 5,000 to 200,000 (preferably 10,000 to 50,000). These detergent compositions further contain 5% to 95% (most preferably 10% to 25%) of certain compatible alcohol sulfate and alkylethyoxy sulfate detergent surfactants and no more than 10% of other incompatible anionic surfactants such as the linear alkyl benzene sulfonates.

U.S. Patent 4,132,680 to Nicol, issued January 2, 1979, also discloses laundry detergent compositions having soil release properties which contain 2% to 95% (preferably 10% to 60%) of a detergent surfactant and 0.15% to 25% (most preferably 1% to 10%) of an ethylene terephthalate/PEG terephthalate (mole ratio of 65:35 to 80:20) soil release polyester having a molecular weight of 10,000 to 50,000, e.g., MILEASE T. These compositions further comprise 0.05% to 15% (most preferably 0.1% to 5%) of a component which disassociates in aqueous solution to yield quaternary ammonium cations having one to three C₈-C₂₄ alkyl groups. These cations are taught by Nicol to improve the deposition of the soil release polyester on the laundered fabric. See column 11, lines 14-21.

B. Use of polyesters in rinse-added products to impart soil release properties

Canadian Patent 1,100,262 to Becker et al, issued May 55, 1981, discloses fabric softener compositions containing 1% to 80% (preferably 5% to 50%) of a fabric-softening agent such as ditallow dimethyl ammonium chloride in combination with 0.5% to

25% (preferably 1% to 10%) of certain choline fatty acid esters. These softening compositions preferably include 0.5% to 10% (preferably 1% to 5%) of an ethylene terephthalate/PEG terephthalate soil release polyester such as PERMALOSE or ZELCON.

5 U.S. Patent 3,893,929 to Basadur, issued July 8, 1975, discloses rinse-added acidic solutions containing a soil release agent made from a dibasic carboxylic acid (preferably terephthalic acid), a polyalkylene glycol (preferably a PEG having a molecular weight of 1,300 to 1,800) and an alkylene glycol (ethylene, 10 propylene or butylene glycol). Preferred soil release agents have a molecular weight of from 3,000 to 5,000. Cationic fabric softeners such as ditallow dimethyl ammonium chloride can be included in these compositions, but are said to be not preferred "since they tend to retard the deposition of the soil release 15 agent on the polyester fibers at acidic pH." See column 7, lines 54-59.

U.S. Patent 3,712,873 to Zenk, issued January 23, 1973, discloses textile treating compositions applied by spraying or padding which comprise 1% to 5% of a soil release polyester of the 20 type disclosed in the Basadur patent. These compositions can additionally contain up to 4% of a quaternary ammonium compound having one C₁₆-C₂₂ alkyl group. The combination of this quaternary ammonium compound with the polyester is described as improving the soil-release characteristic of the treated fabric. 25 Zenk also states that other quaternary ammonium compounds, such as ditallow dimethyl ammonium chloride, did not give the same superior performance. See column 3, lines 57-61.

C. Use of polyesters in dryer-added products to impart soil release properties

30 U.S. Patent 4,238,531 to Rudy et al, issued December 9, 1980, discloses dryer-added products which contain a "distributing agent" such as polyethylene glycol and an adjuvant applied to the fabric which can be a soil release agent. Soil release agents disclosed include polyacrylic resins, polyvinyl alcohol and 35 PERMALOSE TG polyesters (see Example 8).

D. Use of polyesters in fabric or textile treating solutions which are heat cured to impart soil release and/or antistatic properties

U.S. Patent 3,512,920 to Dunlap, issued May 9, 1970, discloses low molecular weight alkylene glycol/polyalkylene glycol terephthalic acid polyesters which are used in resin treating baths containing starch or cellulose derivatives to impart soil release properties to cotton/polyester fabrics after heat curing. The alkylene glycols which can be used to make these polyesters include ethylene glycol, 1,2-propylene glycol, 1,3-propylene glycol, butylene glycol and mixtures thereof. The polyalkylene glycols which can be used include PEG, polybutylene glycol and mixtures thereof which have an average molecular weight of 200 to 20,000 (preferably 1,000 to 5,000).

U.S. Patent 3,416,952 to McIntyre et al, issued December 17, 1968, discloses polyester antistatic agents which can contain a water-solvatable polymeric group such as a polyoxyalkylene group having an average molecular weight of from 300 to 6,000. Preferred polyoxyalkylene groups are the PEG's having an average molecular weight of from 1,000 to 4,000. Treatment is carried out by applying an aqueous dispersion of the polyester in the presence of an antioxidant, followed by heating to a temperature above 90°C to obtain a durable coating of the polyester on the treated article. Example 6 discloses one such polyester formed by the catalyzed reaction of dimethyl terephthalate, ethylene glycol and an O-methyl poly(oxyethylene)glycol having an average molecular weight of 350. A 20% solution of this polyester in benzyl alcohol was used to impart antistatic properties to a polyester fabric. Example 7 discloses a 20% aqueous solution of a similar polyester used to impart antistatic properties to a polyester fabric.

U.S. Patent 4,427,557 to Stockburger, issued January 24, 1984, discloses low molecular weight copolyesters (2,000 to 10,000) formed by the reaction of ethylene glycol, a PEG having an average molecular weight of 200 to 1,000, an aromatic dicarboxylic acid (e.g., dimethyl terephthalate), and a sulfonated aromatic dicarboxylic acid (e.g., dimethyl 5-sulfoisophthalate). The PEG can be replaced, in part, with monoalkylethers of PEG such as the methyl, ethyl and butyl ethers. A dispersion or solution of the copolyester is applied to the textile material and then heat set at elevated temperatures (90°C to 150°C) to impart durable soil release properties. See also the McIntyre et al patent, where Example 2 discloses a random copolyester used to impart antistatic

properties which is formed by reacting dimethyl terephthalate, sodium dimethyl sulfoisophthalate, ethylene glycol and a PEG having an average molecular weight of 1,540.

5 In addition, there are several disclosures in the art of polyesters, more particularly their lower molecular weight oligomers, capable of acting as sra's in laundry products. The earlier disclosures relate to modified polyester-type materials which are not necessarily oligomeric and which contain segments without particular end-caps. They derive from ethylene glycol/
10 dimethyl terephthalate randomly interspersed with polyether segments deriving from polyethylene glycol. See, for example, U.S. Patent 3,962,152, Nicol et al, issued June 8, 1976, U.S. Patent 4,116,885, Derstadt et al, issued September 7, 1978, Canadian Patent 1,100,262, Becker et al, issued May 5, 1981, U.S.
15 Patent 4,238,531, Rudy et al, issued December 9, 1980, and British Patent Application 2,172,608, Crossin, published September 24, 1986.

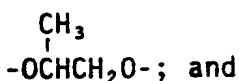
More recent developments in the field of sra's for laundry detergent applications include certain end-capped ester oligomers,
20 such those generally disclosed in United States patents to Gosselink: see, for example, U.S. Patent 4,702,857, issued October 27, 1987, U.S. Patent 4,721,580, issued January 26, 1988 and U.S. Patent 4,877,896, Maldonado, Trinh and Gosselink, issued October 31, 1989.

25 SUMMARY OF THE INVENTION

The present invention encompasses soil release agents which comprise the oligomeric esterification product of a reaction mixture which comprises:

- 30 (a) optionally, but preferably, a source of C_1 - C_4 alkoxy-terminated (preferably, methoxy-terminated) polyethoxy units $R^1-(OCH_2CH_2)_x-O-$ or, optionally, mixtures of said terminated polyethoxy units which incorporate small amounts of propoxy units;
- 35 (b) a source of terephthaloyl units or, optionally, mixtures of terephthaloyl and small amounts of isophthaloyl units;
- (c) a source of poly(oxyethylene)oxy units $-(OCH_2CH_2)_y-O-$;
- (d) a source of oxyiso-propyleneoxy units

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(e) a source of oxyethyleneoxy units $-\text{OCH}_2\text{CH}_2\text{O}-$;
said soil release agents being further characterized by having a
mole ratio of oxyethyleneoxy units:oxyiso-propyleneoxy units of at
least about 0.5:1.

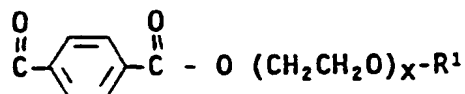
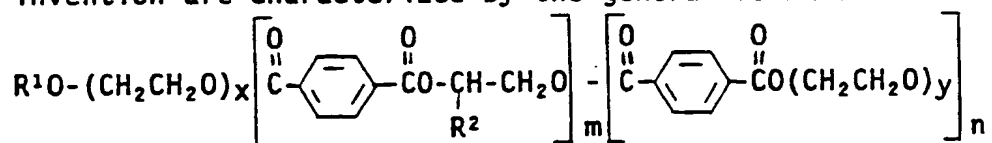
Thus, the soil release agents herein comprise, for example,
the esterification reaction product of a reaction mixture
comprising:

- (a) $\text{CH}_3(\text{OCH}_2\text{CH}_2)_{16}\text{OH}$;
- (b) dimethyl terephthalate;
- (c) polyethylene glycol 1500 (E_{34});
- (d) 1,2-propylene glycol; and
- (e) ethylene glycol;

wherein the mole ratio of oxyethyleneoxy units:oxyiso-propyleneoxy
units is at least about 0.5:1, preferably at least about 1.25:1.

Such soil release agents differ from the sra's disclosed by
Gosselink and Diehl, U.S. Patent 4,711,730, cited above, in that
they contain oxyethyleneoxy units. The sra's of this invention
unexpectedly exhibit better performance than those of the '730
patent.

While not intending to be limited by theoretical or struc-
tural consideration, it is believed that the preferred sra's of
this invention are characterized by the general formula:



wherein R^1 is lower (e.g., C_1 - C_4) alkyl, especially methyl; and R^2
is a mixture of both H and CH_3 (i.e., both ethylene and
isopropylene moieties are present in the molecular structure) to
provide a mole ratio of oxyethyleneoxy:oxyisopropyleneoxy of at
least about 0.5:1, preferably at least about 1.25:1.

In the formula depicted, x, y, m and n are integers within
the following ranges:

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	<u>Broad</u>	<u>Preferred</u>	<u>Most Preferred</u>
x	6-100	6-43	12-30
y	6-100	12-77	12-50
m	0.75-30	1.5-25	2.25-20
5 n	0.25-20	0.5-15	0.75-12
$\frac{m+n+1}{n+1}$ *	1-5	1.2-4.5	1.5-4

*This term indicates the average number of adjacent terephthalate units before interruption by a PEG unit.

10 It is to be understood that the mole ratio of oxyethyleneoxy: oxypropyleneoxy units can be varied to meet the needs of the formulator. For example, for use with fabric softeners, this ratio is preferably at least about 0.75:1, more preferably at least about 1.25:1. For use in liquid detergents, some product
15 haziness may occur at these ratios, so the formulator may elect to select a somewhat lower ratio, e.g., 0.5:1.

The invention also encompasses laundry compositions such as detergents, softeners, rinse aids, and the like, comprising at least about 0.1%, preferably from about 0.2% to about 10% by
20 weight, of the foregoing sra's.

Preferred fabric softener compositions herein typically comprise from about 0.3% to about 3% by weight of the sra and from about 3% to about 25% by weight of a fabric softener component.

A dilutable liquid fabric softener composition concentrate
25 comprises:

- (a) from about 10% to about 32% by weight of a cationic fabric softener;
- (b) from about 4% to about 20% by weight of an imidazolinium fabric softener; and
- 30 (c) from about 1% to about 5% by weight of the sra.

Typical laundry detergent compositions herein comprise conventional deterative surfactants, optional builders, optional carriers, and from about 0.1% to about 10% by weight of the sra. Preferred laundry detergents comprise from about 0.3% to about 3%
35 by weight of said soil release agent and at least about 3%, preferably from about 3% to about 20% by weight of a fatty acid polyhydroxy amide surfactant, especially C₁₂-C₁₈ fatty acid N-methylglucamide.

The invention also encompasses a method for providing a soil release finish on fabrics by contacting said fabrics with an aqueous medium containing at least about 2 ppm of the foregoing sra's. In a preferred mode, the method comprises contacting the fabrics with an aqueous bath comprising at least 3 ppm (preferably from about 4 ppm to about 25 ppm) of the foregoing sra's and at least about 10 ppm (preferably from about 30 ppm to about 100 ppm) of a cationic fabric softener for a period of at least about 1 minute (preferably from about 1 minute to about 10 minutes) before separating the fabrics from the aqueous bath. (It will be appreciated that even lower levels of the sra's can be effective with multicycle treatments.) It will be appreciated that such methods can readily be carried out during the rinse cycle in a conventional automatic washing machine.

All percentages, ratios and proportions herein are by weight, unless otherwise specified.

DETAILED DESCRIPTION OF THE INVENTION

The sra's of the present invention are prepared by esterification of the hydroxyl- and carboxylate-substituted reactants disclosed hereinabove. The following Examples further illustrate the preparation of sra's according to this invention, but are not intended to be limiting thereof.

EXAMPLE I

Synthesis of a Polymer of Poly(Ethylene Glycol) Methyl Ether of MW 750, Dimethyl Terephthalate, Poly(Ethylene Glycol) of MW 1500, Ethylene Glycol, and Propylene Glycol - To a 250 ml, three-neck, round bottom flask equipped with a magnetic stirring bar, modified Claisen head, condenser (set for distillation), thermometer, and temperature controller (THERM-O-WATCH, I²R) is added poly(ethylene glycol) methyl ether of MW 750 (Aldrich, 50.0 g, 0.067 mol), dimethyl terephthalate (35.6 g, 0.183 mol), poly(ethylene glycol) of MW 1500 (Aldrich, 50.0 g, 0.033 mol), ethylene glycol (Baker, 7.2 g, 0.116 mol), 1,2-propylene glycol (Fisher, 8.9 g, 0.117 mol), hydrated monobutyltin oxide (M&T Chemicals, 0.30 g, 0.2% of total reaction weight), and butylated hydroxytoluene (Calbiochem, 0.15 g, 0.1% of total reaction weight). This mixture is heated to 180°C and maintained at that temperature overnight under argon as methanol and water distill from the reaction vessel. A ¹³C-NMR(DMSO-d₆) shows a residual

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resonance for methyl esters at -52 ppm. The temperature is raised to 200°C for 5 hours, and then additional ethylene glycol (7.2 g, 0.116 mol) and propylene glycol (8.9 g, 0.117 mol) are added. The temperature is lowered to 190°C, where it is maintained overnight. A ^{13}C -NMR(DMSO- d_6) shows this stage of the reaction to be complete by the disappearance of the resonance for methyl esters. The material is transferred to a 1 liter, single neck, round bottom flask and heated gradually over about 20 minutes to 230°C in a Kugelrohr apparatus (Aldrich) at about 1.5 mm Hg and maintained there for 1 hour. The flask is then allowed to air cool quite rapidly to near room temperature under vacuum (~30 min.). The reaction yields 124.1 g of soft brown solid. The ^1H -NMR(DMSO- d_6) shows a very intense resonance at about 3.5 ppm for the poly(oxyethylene) segments, a resonance at about 8.0 ppm for the terephthalates, resonances at about 1.4 ppm for the methyl group of doubly esterified propylene glycol, and at about 4.7 ppm for doubly esterified ethylene glycol. Comparison of the resonances at 1.4 and 4.7 ppm indicates that the mole ratio of ethylene glycol-derived units to propylene glycol-derived units is approximately 2.2:1. This is referred to as the E/P ratio. The ^{13}C -NMR(DMSO- d_6) is also consistent with the desired polymer structure, showing resonances at 70.2 (polyoxyethylene segments), 16.5 ppm (CH_3 of doubly esterified propylene glycol), 63.6 ppm (doubly esterified ethylene glycol), and 58.4 ppm ($\text{CH}_3\text{OCH}_2\text{CH}_2\text{O}-$). The absence of resonances at about 60 ppm for any monoesters of ethylene glycol ($-\text{C}(\text{O})\text{OCH}_2\text{CH}_2\text{OH}$) or at about 20 ppm for the methyl group of one of the isomeric monoesters of propylene glycol ($-\text{C}(\text{O})\text{OCH}(\text{CH}_3)\text{CH}_2\text{OH}$) indicates that the degree of polymerization is high.

An oligomer with a lower E/P ratio may be obtained using the same synthesis conditions except that the initial ratio of ethylene glycol:propylene glycol is reduced. Typically, an initial glycol ratio of about 0.25:1 gives a final E/P ratio of about 0.5:1.

EXAMPLE II

Polymer of Ethylene Glycol, Dimethyl Terephthalate, Poly(Ethylene Glycol) Methyl Ether of MW 750, Poly(Ethylene Glycol) of MW 1500, and 1,2-Propylene Glycol (With E/P=1.5) - Into a 5 liter, three necked, round bottom flask equipped with magnetic

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stirring, heating mantle, internal thermometer, distillation head, condenser set for distillation, inlet for inert gas, and THERM-O-WATCH (I²R) for temperature control, are placed the following:

		<u>Grams</u>	<u>Moles</u>	<u>Source</u>
5	Ethylene glycol	130.2	2.1	MCB
	Dimethyl terephthalate	640.2	3.3	Aldrich
	Poly(ethylene glycol)	300	0.4	Union Carbide
	methyl ether MW 750			
	Poly(ethylene glycol)	1500	1.0	Union Carbide
10	of MW 1500			
	1,2-propylene glycol	322	4.2	Fisher
	Hydrated monobutyltin oxide	5.5		M&T Chem
	(FASCAT 4100)			
	Butylated hydroxy toluene (BHT)	3.2		Calbiochem

- 15 The system is stirred as the temperature is gradually raised to 185°C and held there for 28 hours as methanol distills from the reaction. Then a fritted glass inlet tube is inserted to near the bottom of the flask and inert gas is passed through at a high rate with the temperature gradually raised to 240°C. This is continued
- 20 for approximately 13 hours. The resulting polymer is allowed to cool to give about 2400 g of a soft solid which is mostly soluble in water at room temperature when tested by stirring overnight at a 10% solids level. The ¹H-NMR(d₆-DMSO) shows a very intense resonance at about 3.45 ppm for the polyoxyethylene segments, a
- 25 complex resonance at about 8.05 ppm for the terephthalates, resonances at about 1.4 ppm for the methyl group of doubly esterified propylene glycol, and at about 4.7 ppm for doubly esterified ethylene glycol. Comparison of the resonances at 1.4 and 4.7 ppm indicates that the mole ratio of ethylene glycol-
- 30 derived units to propylene glycol-derived units is approximately 1.5:1. This is referred to as the E/P ratio. The ¹³C-NMR(d₆-DMSO) is also consistent with the desired polymer structure, showing resonances at 70.2 ppm (polyoxyethylene segments), 16 ppm (CH₃ of doubly esterified propylene glycol), 63.6 ppm (doubly esterified ethylene glycol), and a very tiny peak at 58 ppm (CH₃OCH₂O-). The virtual absence of resonances at about 60 ppm for any monoesters of ethylene glycol (-C(O)OCH₂CH₂OH) or at about
- 35 20 ppm for one of the isomeric monoesters of propylene glycol

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((-C(O)OCH(CH₃)CH₂OH) indicates that the degree of polymerization is high.

EXAMPLE III

5 Polymer of Ethylene Glycol, Dimethyl Terephthalate,
 Poly(Ethylene Glycol) Methyl Ether of MW 750, Poly(Ethylene
 Glycol) of MW 1500, and 1,2-Propylene Glycol - Into a 5 liter,
 three necked, round bottom flask equipped with magnetic stirring,
 heating mantle, internal thermometer, distillation head, condenser
 set for distillation, inlet for inert gas, and THERM-O-WATCH (I²R)
 10 for temperature control, are placed the following:

	<u>Grams</u>	<u>Moles</u>	<u>Source</u>
Ethylene glycol	408	6.58	Fisher
Dimethyl terephthalate	1024	5.28	Aldrich
Poly(ethylene glycol)	480	0.64	Aldrich
15 methyl ether MW 750			
Poly(ethylene glycol)	2400	1.60	Aldrich
of MW 1500			
1,2-propylene glycol	510	6.71	Mallinkrodt
Hydrated monobutyltin oxide	3		M&T Chem
20 (FASCAT 4100)			
Butylated hydroxy toluene (BHT)	3		Calbiochem

 The system is stirred as the temperature is gradually raised
 from 175°C to 195°C over a 36 hour period as 290 g of distillate
 (mostly methanol) is collected. The temperature is then raised to
 25 210°C for 18 hours as more distillate is collected. Then a
 fritted glass inlet tube is inserted to near the bottom of the
 flask and inert gas is passed through at a high rate with the
 temperature maintained at 200°C. This is continued for
 approximately 4 days as a small amount of additional distillate
 30 collects. The resulting polymer is allowed to cool to give about
 3800 g of a soft solid which is about 65% soluble in water at room
 temperature when tested by stirring overnight at a 10% solids
 level. (In lower solids-content solutions, the fraction dissolv-
 ing appears to be considerably higher.) The ¹H-NMR(d₆-DMSO) shows
 35 a very intense resonance at about 3.45 ppm for the polyoxyethylene
 segments, a complex resonance at about 8.05 ppm for the tere-
 phthalates, resonances at about 1.4 ppm for the methyl group for
 doubly esterified propylene glycol, and at about 4.7 ppm for
 doubly esterified ethylene glycol. Comparison of the resonances

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at 1.4 and 4.7 ppm indicates that the mole ratio of ethylene glycol-derived units to propylene glycol-derived units is approximately 2.6:1. This is referred to as the E/P ratio. The ^{13}C -NMR(d_6 -DMSO) is also consistent with the desired polymer structure, showing resonances at 70.2 ppm (polyoxyethylene segments), 16 ppm (CH_3 of doubly esterified propylene glycol), 63.6 ppm (doubly esterified ethylene glycol), and a very tiny peak at 58 ppm ($\text{CH}_3\text{OCH}_2\text{CH}_2\text{O}-$). The virtual absence of resonances at about 60 ppm for any monoesters of ethylene glycol ($-\text{C}(\text{O})\text{OCH}_2\text{CH}_2\text{OH}$) or at about 20 ppm for one of the isomeric monoesters of propylene glycol ($-\text{C}(\text{O})\text{OCH}(\text{CH}_3)\text{CH}_2\text{OH}$) indicates that the degree of polymerization is high.

Fabric Treatment Compositions

The sra's according to this invention can be employed in a variety of circumstances where it is desired to impart a soil release finish to fabrics, especially in a laundering operation. For example, the sra's herein can be added directly to a laundry or rinse bath of an automatic washing machine. Alternatively, the sra's can be sprayed onto fabrics during an ironing operation. In another mode, the sra's can be deposited onto fabrics during a laundry drying operation in an automatic clothes dryer.

In a preferred mode, the sra's herein are deposited onto fabrics from an aqueous bath containing a fabric softener, such as the cationic fabric softeners well-known in the art. Indeed, various sra's can be selected from those disclosed herein which are quite compatible with cationics and do not disadvantageously increase the viscosities of even the "triple-concentrate" liquid fabric softener products that have recently come onto the market. In general, the lower molecular weight sra's will result in lesser increases in viscosities. Accordingly, preferred compositions herein provide both a fabric softener component and an sra component, and are designed to provide a fabric softening (and antistatic) benefit concurrently with a soil release conditioning. The following is intended to assist the formulator in the manufacture of combined fabric softener/soil release compositions, but is not intended to be limiting thereof.

Liquid Fabric Softeners - The liquid fabric softener compositions of the present invention comprise an effective amount of the sra's hereinabove defined. What is an "effective amount" will

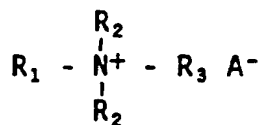
depend upon the particular sra's used, the particular type of fabric softener formulation and the benefits desired. Usually, the sra's are effective when included in an amount from about 0.01 to about 10% by weight of the composition. In terms of soil release benefits, preferred fabric softener compositions can comprise from about 0.1 to about 5% by weight of the sra's, but typically comprise from about 0.3 to about 3% by weight of these compounds.

The fabric softener compositions of the present invention further comprise from about 2 to about 50% (preferably from about 3 to about 25%) by weight fabric softener components. For regular strength (1X) fabric softener compositions, the fabric softener component typically comprises from about 3 to about 10% by weight of the composition. For concentrated (e.g., 3X) fabric softener compositions, the fabric softener component typically comprises from about 15 to about 25% by weight of the composition.

The fabric softener component typically comprises a mono- or di(higher alkyl) quaternary ammonium salt or mixtures of such salts. See U.S. Patent 3,928,213 to Temple et al, issued December 23, 1975, especially column 2, line 57 to column 4, line 34, and U.S. Patent 4,399,045 to Burns, issued August 16, 1983, especially column 4, line 23 to column 7, line 2 (herein incorporated by reference), which disclose suitable quaternary ammonium salts. By "higher alkyl" as used in the context of the quaternary ammonium salts herein is meant alkyl groups having from 8 to 30 carbon atoms, preferably from 12 to 22 carbon atoms. Examples of such conventional quaternary ammonium salts include:

1. mononitrogen quaternary ammonium salts having the formula:

30



wherein R_1 is an aliphatic C_{12} - C_{22} hydrocarbon group; R_2 is a C_1 - C_4 saturated alkyl or hydroxyalkyl group. R_3 is selected from R^1 (preferred) or R_2 groups and A is an anion such as chloride, bromide or methyl sulfate.

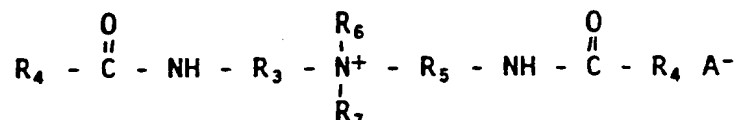
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Examples of suitable mononitrogen quaternary ammonium salts are mono tallowtrimethylammonium chloride (MTTMAC), ditallowdi-

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methyammonium chloride (DTDMAC), ditallowdimethylammonium methyl sulfate, di(hydrogenated tallow)dimethylammonium chloride, dibehenyl dimethylammonium chloride, dihexadecyldimethylammonium chloride, dioctadecyldimethylammonium chloride, dieicosyldimethylammonium chloride, didocosyldimethylammonium chloride; di(hydrogenated tallow)dimethylammonium methyl sulfate; dihexadecyldiethylammonium chloride; ditallowdipropylammonium bromide; di(coconutalkyl)dimethylammonium chloride; and mixtures thereof;

2. diamide quaternary ammonium salts having the formula:



wherein R_4 is an aliphatic C_{12} - C_{22} hydrocarbon group; R_3 and R_5 are each divalent alkylene group having 1 to 3 carbon atoms; R_6 is a C_1 - C_4 saturated alkyl or hydroxyalkyl group; R_7 is R_6 or the moiety $(C_aH_{2a}O)_bH$, wherein a is 2 or 3 and b is from 1 to about 5; and A is an anion.

Examples of suitable diamide quaternary ammonium salts are methylbis(tallowamidoethyl)(2-hydroxyethyl)ammonium methyl sulfate, methylbis(hydrogenated tallowamidoethyl)(2-hydroxyethyl)ammonium methyl sulfate, and bis(2-hydrogenated tallowamidoethyl)ethoxylatedammonium methyl sulfate; these materials are available from Sherex Chemical Company under the trade names VARISOFT 222, VARISOFT 220 and VARISOFT 110;

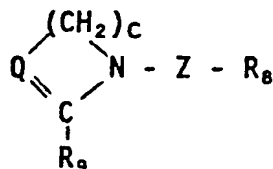
3. quaternary imidazolinium salts such as 1-methyl-1-tallowamido-ethyl-2-tallowimidazolinium methyl sulfate (sold under the trade name VARISOFT 475), 1-methyl-1-(hydrogenated tallowamidoethyl)-2-tallowimidizolium methyl sulfate (sold under the trade name VARISOFT 445), 1-ethylene-bis(2-tallow-1-methylimidazolinium methylsulfate) (sold under the trade name VARISOFT 6112); and 1-methyl-2-tallow-3[tallowamidoethyltallowylamino)ethyl]imidazolinium methylsulfate (sold under the trade name VARISOFT 3012).

For concentrated fabric softener compositions, a preferred fabric softener component comprises: (A) from about 2 to about 15% by weight mononitrogen quaternary ammonium salts; (B) from 0 to about 14% by weight diamide quaternary ammonium salts; (C) from about 2 to about 13% by weight quaternary imidazolinium salts; the

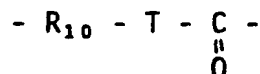
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total amount of salts A, B and C being from about 15 to about 22.5% by weight. See U.S. Patent 4,399,045 to Burns, issued August 16, 1983, which is incorporated by reference.

The fabric softener component can also comprise certain di(higher alkyl) cyclic amines, typically as a mixture with a quaternary ammonium salt(s). These cyclic amines have the formula:



wherein c is 2 or 3, preferably 2; R₈ and R₉ are, independently, a C₈-C₃₀ alkyl or alkenyl group, preferably C₁₁-C₂₂ alkyl, more preferably C₁₅-C₁₈ alkyl, or mixtures of such alkyl radicals, such as those obtained from coconut oil, "soft" (nonhardened) tallow, and hardened tallow; Q is CH or N, preferably N; Z is



wherein T is O or NR₁₁, R₁₁ being H or C₁-C₄ alkyl, preferably H; and R₁₀ is a divalent C₁-C₃ alkylene or (C₂H₄O)_d group, wherein d is a number of from 1 to 8, or Z is R₁₀.

Specific examples of such amines are as follows: 1-tallow-amidoethyl-2-tallowimidazoline; 1-(2-C₁₄₋₁₈-alkyl-amidoethyl)-2-C₁₃-C₁₇-alkyl-4,5-dihydro-imidazole; 1-stearylamidopropyl-2-stearylimidazoline; and 1-tallowamidobutyl-2-tallowpiperidine.

These amides and methods for their preparation are fully described in British Application 8,508,130, filed March 28, 1985 by Koenig and deBuzzacarini which is herein incorporated by reference. (See also U.S. Patent 4,711,730, column 28.)

C. Optional Ingredients

1. Acids and Bases - When cyclic amines are present in the fabric softener component, the pH of the fabric softener composition is important for proper dispersion of the amines. Moreover, a somewhat acidic pH is preferred for hydrolytic stability of the soil release compounds of the present invention. Therefore, acids and/or bases can be added to the composition to adjust its pH. The amount of acid or base should be such that the pH of the dispersion, after mixing, is in the range from about 2.5 to about 6.5.

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Examples of suitable acids include the inorganic mineral acids, carboxylic acids, in particular the low molecular weight (C_1 - C_3) carboxylic acids, and alkanesulfonic acids.

5 Suitable inorganic acids include HCl , H_2SO_4 , HNO_3 and H_3PO_4 .
Suitable organic acids include formic, acetic, methanesulfonic and ethanesulfonic acid. Preferred acids are hydrochloric, phosphoric, formic and methanesulfonic acid.

Suitable bases include $NaOH$ and Na_2CO_3 .

10 2. Organic solvent - The fabric softener compositions of the present invention can be formulated without the use of any organic solvent. However, the presence of organic solvents (for example, low molecular weight, water miscible aliphatic alcohols) does not harm the storage stability, the viscosity, or the softening performance of the compositions. Examples of such
15 solvents include ethanol and isopropanol.

Typically, the quaternary ammonium salt(s) (or cyclic amine) will be obtained from a supplier of bulk chemicals in solid form or as a solution in an organic solvent, e.g., isopropanol. There is no need to remove such a solvent in making the compositions.
20 Indeed, additional solvent can be added, if this is deemed desirable.

3. Optional Nonionics - The fabric softener compositions optionally contain nonionics as have been disclosed for use in softener compositions. Such nonionics and the usage levels have been disclosed in U.S. Patent 4,454,049, to MacGilp et al, issued
25 June 12, 1984, which is incorporated by reference.

Specific examples of nonionics suitable for the fabric softener compositions herein include glycerol esters (e.g., glycerol monostearate), fatty alcohols (e.g., stearyl alcohol),
30 and alkoxylated fatty alcohols. The nonionic, if used, is typically used at a level in the range of from about 0.5 to about 10% by weight of the composition.

Although generally considered as having fabric softening properties, the nonionics are not considered part of the fabric softening component for the purposes of calculating the amount of
35 fabric softening component in the composition.

4. Optional Silicone Component - The fabric softening composition optionally contains an aqueous emulsion of a predominantly linear polydialkyl or alkyl aryl siloxane in which the

alkyl groups can have from one to five carbon atoms and can be wholly or partially fluorinated. Suitable silicones are polydimethyl siloxanes having a viscosity at 25°C in the range from about 100 to about 100,000 centistokes, preferably in the range from about 1,000 to about 12,000 centistokes.

The ionic charge characteristics of the silicone as used in the combination can be important in determining both the extent of deposition and the evenness of distribution of the silicone and hence the properties of a fabric treated therewith.

Silicones having cationic character show an enhanced tendency to deposit. Silicones found to be of value in providing fabric feel benefits have a predominantly linear character and are preferably polydialkylsiloxanes in which the alkyl group is most commonly methyl. Such silicone polymers are frequently manufactured commercially by emulsion polymerization using a strong acid or strong alkali catalyst in the presence of a nonionic or mixed nonionic-anionic emulsifier system.

The optional silicone component also embraces a silicone of cationic character which is defined as being one of: (a) a predominantly linear poly di C₁-C₅ alkyl- or C₁-alkyl, aryl-polysiloxane, prepared by emulsion polymerization using a cationic surfactant as emulsifier; (b) an alpha-omega-di quaternized di C₁-C₅ or C₁-C₅ alkyl, aryl siloxane polymer; or (c) an amino-functional di (C₁-C₅ alkyl or alkyl aryl siloxane polymer in which the amino group may be substituted and may be quaternized and in which the degree of substitution (d.s.) lies in the range 0.001 to 0.2, preferably 0.01 to 0.073; provided that the viscosity at 25°C of the silicone is from about 100 to about 100,000 centistokes.

The fabric softening compositions herein can contain up to about 10%, preferably from about 0.1% to about 5%, of the silicone component.

5. Other Optional Ingredients - In order to further improve the stability of the fabric softener compositions herein, and further adjust their viscosities, these compositions can contain relatively small amounts of electrolytes (e.g., 0.1%-3%), such as NaCl, KBr, LiCl, MgCl₂ or CaCl₂.

The fabric softener compositions can also optionally contain other ingredients known to be suitable for use in textile softeners. Such adjuvants include perfumes, preservatives, germicides,

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colorants, dyes, fungicides, stabilizers, brighteners and opacifiers. These adjuvants, if used, are normally added at their conventional levels (ca. 0.1%-5%). However, in the case of composition ingredients utilized for a fabric treatment effect, e.g., perfumes, these materials can be added at higher than normal levels, corresponding to the degree of concentration of the product.

The balance of the liquid fabric softener compositions of the present invention is water.

The following illustrates liquid compositions of the foregoing type.

EXAMPLE IV

A fabric softener base composition is prepared from the following ingredients:

<u>Ingredient</u>	<u>Wt. %</u>
Ditallowdimethylammonium chloride	4.33
1-methyl-1-tallowamidoethyl-2-tallow-imidazolinium methyl sulfate (VARISOFT 475)	1.0
Ethanol	0.7
Isopropanol	0.1
Perfume	0.42
Dye	0.1
Minors*	up to 0.1
Water	Balance

*preservative, NaCl, NaOH, H₂SO₄, antioxidant solution.

To this base composition is added 1% by weight of the sra's of Examples I and II, respectively, to provide fabric softening/sra compositions IVA and IVB.

EXAMPLES V-VIII

Regular strength and concentrated fabric softener base compositions are prepared from the following ingredients:

<u>Ingredient</u>	<u>Wt. %</u>			
	V	VI	VII	VIII
Ditallowdimethylammonium chloride	3.65	7.7	2.33	7.0
1-tallowamidoethyl-2-tallowimidazoline	3.65	14.3	4.33	3.0
Tallowtrimethylammonium chloride	0.5	0.5	---	---
Polydimethylsiloxane (viscosity 5,000 centistokes)	0.2	0.6	1.33	4.0

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Perfume	0.25	0.45	0.25	0.45
Minors*	0.13	0.13	0.13	0.13
HCl	---	to pH 4	---	---
Water	---	Balance	---	---

5 *CaCl₂, dye, bactericide

To regular strength base compositions V and VII are added 0.5% by weight of the sra's of Examples I and III, respectively. To concentrated base compositions VI and VIII are added 1.5% by weight of the sra's of Examples I and II, respectively.

10

EXAMPLE IX

A concentrated fabric softener base composition is prepared from the following ingredients:

	<u>Ingredient</u>	<u>Wt. %</u>
15	Dihydrogenated tallow dimethylammonium chloride	13
	1-methyl-1-tallowamidoethyl-2-tallowimidazolinium methyl sulfate	3
	Polar Brilliant Blue dye	80 ppm
	CaCl ₂	0.265
20	Perfume	0.75
	Ethanol	0.92
	Isopropanol	1.36
	Water	Balance

25 To this concentrated base composition is added 1.5% by weight of the sra's of Examples I, II and III, respectively, to provide concentrated softener compositions plus sra IXA, IXB and IXC.

EXAMPLE X

A preferred softener composition is as follows.

	<u>Ingredient</u>	<u>Wt. % of Final Formula</u>
30	<u>Premix</u>	
	DTDMAC	4.00
	MTTMAC	0.67
	VARISOFT 475*	2.00
	<u>Water Seat</u>	
35	Deionized water	Balance
	Silicone DC-1520 (antifoam)	0.02
	HCl**	0.35
	Lytron 621 (dye)	0.75
	SRA***	2.25

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Post Addition

KATHON (preservative)	0.04
Poly(dimethyl siloxane)****	0.20
Perfume	0.30

5 * Imidazolinium fabric softener

 ** Enough to have the pH of final product at 3-3.5.

 *** Prepared in the manner of Example I; E/P ratio 1.5.

 ****A 55% polydimethyl siloxane (350 cps) emulsion in water.

 The Premix is blended with the Water Seat, then combined with
10 the Post Addition mix.

EXAMPLE XI

Using the ingredients illustrated in Example X, a 3X concentrated fabric softener is prepared, as follows.

	<u>Ingredient</u>	<u>Wt. % of Final Formula</u>
15	<u>Premix</u>	
	DTDMAC	14.67
	VARISOFT 475	6.00
	<u>Water Seat</u>	
	Deionized water	Balance
20	Silicone DC-1520	0.02
	HCl*	0.35
	Lytron 621 (dye)	0.75
	SRA (E/P 1.5 per Example II)	1.50
	<u>Post Addition</u>	
25	KATHON	0.04
	Poly(dimethyl siloxane)	0.54
	Perfume	1.05

*Enough to have the pH of final product at 3-3.5.

30 Laundry Detergents - The sra's of the present invention are also useful in certain laundry detergent compositions to provide soil release properties. These compositions can be used as laundry detergents, laundry additives, and laundry pre-treatments.

35 The laundry detergent compositions of the present invention comprise a soil release component which contains an effective amount of the sra's previously defined. What is an "effective amount" will depend upon the particular sra's used, the particular type of detergent formulation (liquid, granular, etc.) and the benefits desired. Usually, the sra's are effective when included in an amount from about 0.01 to about 10% by weight of the

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composition. In terms of soil release benefits, preferred laundry detergent compositions can comprise from about 0.1 to about 5% by weight of the sra's, but typically comprise from about 0.3 to about 3% by weight of these compounds.

5 For granular detergent formulations, the sra component typically comprises the sra compounds, plus any protective enrobing material. In making granular detergent formulations, the sra could be exposed to highly alkaline materials such as NaOH and KOH. The sra's, in particular those having shorter backbones, can
10 be degraded by alkaline environments, especially those above a pH of about 8.5. Accordingly, the sra's are preferably enrobed in a material which protects them from the alkaline environment of a granular detergent formulation yet permits the sra's to be dispersed in the laundering operation.

15 Suitable enrobing materials include the nonionic surfactants, polyethylene glycols (PEG), fatty acids, fatty acid esters of diols and polyols, anionic surfactants, film forming polymers and mixtures of these materials. Examples of suitable nonionic
20 surfactant enrobing materials include some of those described hereinafter as also being useful deterative surfactants in the compositions. Examples of suitable PEG enrobing materials are those having an average M.W. of from about 2,000 to 15,000, preferably from about 3,000 to about 10,000 and most preferably from about 4,000 to about 8,000. Examples of suitable fatty acid
25 enrobing materials are the higher fatty acids having from 12 to 18 carbon atoms. Examples of suitable fatty acid ester enrobing materials include the sorbitan fatty acid esters (e.g., sorbitan monolaurate). Other examples of suitable enrobing materials, including anionic surfactants and film forming polymers, are
30 disclosed in U.S. Patent 4,486,327 to Murphy et al, issued December 4, 1984, which is incorporated by reference. The sra's can be enrobed according to the methods disclosed in this Murphy et al patent.

35 For liquid detergent formulations, the sra component can be comprised entirely of sra's or can further include a water-soluble organic solvent or a hydrotrope to aid in dissolving the sra's. Suitable organic solvents are usually aromatic and can include ethyl benzoate, phenoxyethanol, methyl-o-toluate, 2-methoxybenzyl

alcohol and pyrrolidone. Suitable hydrotropes include the methyl capped PEG's and shorter backbone polyesters. These short backbone polyesters are more water-soluble, and, accordingly, can function as hydrotropes for the longer backbone, less water-insoluble sra's.

The amount, or even the need for, organic solvents or hydrotropes to prepare liquid detergent formulations containing the sra's of the present invention will depend upon the sra's used, especially what fraction thereof is water-soluble, the ingredients present in the laundry detergent system, and whether an isotropic, homogeneous liquid is desired. For isotropic liquid detergent formulations, the sra's need to be dissolved as much as possible which sometimes requires the use of organic solvents or hydrotropes. Also, it is believed that dissolving the sra's in liquid detergent formulations can make them more effective as soil release agents by facilitating dissolution in the wash liquor and thereby the adsorption on target fabrics.

Laundry compositions of the present invention preferably comprise from about 5 to about 75% by weight of a noninterfering, preferably nonionic deterative surfactant. Preferably, the nonionic deterative surfactant comprises from about 10 to about 40% by weight of the composition, and most preferably from about 15 to about 30% by weight.

Suitable nonionic surfactants for use in laundry compositions of the present invention are generally disclosed in U.S. Patent 3,929,678 to Laughlin et al, issued December 30, 1975 at column 13, line 14 through column 16, line 6 (herein incorporated by reference). Classes of nonionic surfactants included are:

1. The polyethylene oxide condensates of alkyl phenols. Examples of compounds of this type include nonyl phenol condensed with about 9.5 moles of ethylene oxide per mole of nonyl phenol; dodecylphenol condensed with about 12 moles of ethylene oxide per mole of phenol. Such materials are available as IGEPAL CO-630, marketed by the GAF Corporation, and Triton X-45, X-114, X-100, and X-102, all marketed by the Rohm & Haas Company.

2. The condensation products of aliphatic alcohols with from about 1 to about 25 moles of ethylene oxide. The alkyl chain of the aliphatic alcohol can either be straight or branched,

primary or secondary, and generally contains from about 8 to about 22 carbon atoms. Examples of such ethoxylated alcohols include the condensation product of myristyl alcohol condensed with about 10 moles of ethylene oxide per mole of alcohol, and the condensation product of about 9 moles of ethylene oxide with coconut alcohol (a mixture of fatty alcohols with alkyl chains varying in length from 10 to 14 carbon atoms). Examples of commercially available nonionic surfactants of this type include TERGITOL 15-S-9, marketed by Union Carbide Corporation, NEODOL 45-9, NEODOL 23-6.5, NEODOL 45-7, and NEODOL 45-4, marketed by Shell Chemical Company, and KYRO EOB, marketed by The Procter & Gamble Company.

3. The condensation products of ethylene oxide with a hydrophobic base formed by the condensation of propylene oxide with propylene glycol. Examples of compounds of this type include certain of the commercially available PLURONIC surfactants, marketed by Wyandotte Chemical Corporation.

4. The condensation products of ethylene oxide with the product resulting from the reaction of propylene oxide and ethylenediamine. Examples of this type of nonionic surfactant include certain of the commercially available TETRONIC compounds, marketed by Wyandotte Chemical Corporation.

5. Semi-polar nonionic detergent surfactants which include water-soluble amine oxides containing one alkyl moiety of from about 10 to 18 carbon atoms and 2 moieties selected from the group consisting of alkyl groups and hydroxyalkyl groups containing from 1 to about 3 carbon atoms; water-soluble phosphine oxides containing one alkyl moiety of from about 10 to 18 carbon atoms and 2 moieties selected from the group consisting of alkyl groups and hydroxyalkyl groups containing from about 1 to 3 carbon atoms; and water-soluble sulfoxides containing one alkyl moiety of from about 10 to 18 carbon atoms and a moiety selected from the group consisting of alkyl and hydroxyalkyl moieties of from about 1 to 3 carbon atoms. Preferred amine oxide detergent surfactants are C₁₀-C₁₈ alkyl dimethyl amine oxide and C₈-C₁₂ alkoxy ethyl dihydroxy ethyl amine oxide.

6. Alkylpolysaccharides disclosed in European Patent Application 70,074 to Ramon A. Llenado, published January 19, 1983, having a hydrophobic group containing from about 6 to about 30 carbon atoms, preferably from about 10 to about 16 carbon atoms

and a polysaccharide, e.g., a polyglycoside, hydrophilic group containing from about 1.5 to about 10, preferably from about 1.5 to about 3, most preferably from about 1.6 to about 2.6 saccharide units.

5 7. Fatty acid amide detergent surfactants (see U.S. Patent 4,711,730, column 17, line 35, for a description of such surfactants).

8. Fatty acid polyhydroxy amide surfactants; see U.S. Patent 2,965,576, issued December 20, 1960; also GB Patent
10 809,060.

Preferred nonionic detergent surfactants for use in laundry compositions of the present invention are the ethoxylated alcohols and alkylphenols, especially the condensation products of C_{12} - C_{14} alcohols with from about 3 to about 7 moles of ethylene oxide per
15 mole of alcohol, e.g., C_{12} - C_{13} alcohol condensed with about 6.5 moles of ethylene oxide per mole of alcohol. N-alkyl glucamine-amide-type surfactants, as described in U.S. Patent 2,965,576 and in British Patent 809,060, E. R. Wilson, constitute another class of preferred nonionic surfactants for use herein.

20 Laundry compositions of the present invention can also comprise from 0 to about 15% by weight (preferably from 0 to about 10% by weight) synthetic anionic detergent surfactants. These synthetic anionic detergent surfactants include the water-soluble salts, typically the alkali metal, ammonium and alkylolammonium
25 salts, of organic sulfuric reaction products having in their molecular structure an alkyl group containing from about 10 to about 20 carbon atoms and a sulfonic acid or sulfuric acid ester group. (Included in the term "alkyl" is the alkyl portion of acyl groups.)

30 Examples of this group of synthetic anionic surfactants are the sodium and potassium alkyl sulfates, especially those obtained by sulfating the higher alcohols (C_8 - C_{18} carbon atoms) and the sodium and potassium alkylbenzenesulfonates in which the alkyl group contains from about 9 to about 15 carbon atoms, in straight
35 chain or branched chain configuration, e.g., those of the type described in U.S. Patents 2,220,099 and 2,477,383. Included in this class of surfactants are the linear straight chain alkylbenzenesulfonates in which the average number of carbon atoms in the alkyl group is from about 11 to 13, abbreviated as C_{11} - C_{13} LAS.

Synthetic anionic surfactants also include: the C₁₀-C₂₂ alkyl polyethoxylate sulfates; the sodium alkyl glyceryl ether sulfonates; the water-soluble salts of esters of alpha-sulfonated fatty acids containing from about 6 to 20 carbon atoms in the fatty acid group and from about 1 to 10 carbon atoms in the ester group; water-soluble salts of 2-acyloxy-alkane-1-sulfonic acids containing from about 2 to 9 carbon atoms in the acyl group and from about 9 to about 23 carbon atoms in the alkane moiety; alkyl ether sulfates containing from about 10 to 20 carbon atoms in the alkyl group and from about 1 to 30 moles of ethylene oxide; water-soluble salts of olefin sulfonates containing from about 12 to 24 carbon atoms; and beta-alkyloxy alkanesulfonates containing from about 1 to 3 carbon atoms in the alkyl group and from about 8 to 20 carbon atoms in the alkane moiety.

The laundry compositions of the present invention can also include ampholytic, zwitterionic and cationic detergent surfactants, as well as alkali metal soaps.

Ampholytic surfactants can be broadly described as aliphatic derivatives of secondary or tertiary amines, or aliphatic derivatives of heterocyclic secondary and tertiary amines in which the aliphatic radical can be straight chain or branched and wherein one of the aliphatic substituents contains from about 8 to 18 carbon atoms and at least one contains an anionic water-solubilizing group, e.g., carboxy, sulfonate, sulfate. See U.S. Patent 3,929,678 to Laughlin et al, issued December 30, 1975 at column 19, lines 18-35 (herein incorporated by reference) for examples of ampholytic surfactants.

Zwitterionic surfactants can be broadly described as derivatives of secondary and tertiary amines, derivatives of heterocyclic secondary and tertiary amines, or derivatives of quaternary ammonium, quaternary phosphonium or tertiary sulfonium compounds. See U.S. Patent 3,929,678 to Laughlin et al, issued December 30, 1975 at column 19, line 38 through column 22, line 48 (herein incorporated by reference) for examples of zwitterionic surfactants.

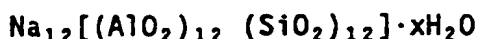
Suitable cationic surfactants are disclosed in U.S. Patent 4,259,217 to Murphy, issued March 31, 1981, herein incorporated by reference.

The alkali metal soaps which are useful include the sodium, potassium, ammonium and alkylammonium salts of higher fatty acids containing from about 8 to about 24 carbon atoms, preferably from about 10 to about 20 carbon atoms.

5 The laundry detergent compositions of the present invention can optionally comprise inorganic or organic detergent builders to assist in mineral hardness control. Such builders will typically comprise up to about 60% by weight of the compositions; built
10 liquid formulations generally comprise from about 1% to about 25% by weight detergency builder, most preferably from about 3% to about 20% by weight, while built granular formulations generally comprise from about 5% to about 50% by weight detergent builder, most preferably from about 10% to about 30% by weight.

15 A wide variety of detergent builders are known in the literature, and it is not intended to reproduce a complete listing of such materials herein. The formulator may refer, for example, to U.S. Patent 4,711,730, beginning at column 19, for a typical listing of such materials. However, for the convenience of the formulator, and not by way of limitation, some representative
20 suitable detergency builders are listed hereinafter.

 Suitable detergent builders include the crystalline aluminosilicate ion exchange materials typically referred to as "Zeolite A", "Zeolite P", and "Zeolite X", especially the zeolites having a
25 particle size from about 0.1 to about 10 microns. Optimum zeolites for builder purposes exhibit a calcium ion exchange rate of at least about 4 grains/gallon/minute/gram/gallon. Amorphous aluminosilicates, especially those having a magnesium ion exchange rate of at least about 1 grain/gallon/minute/gram/gallon are also useful. A method for producing aluminosilicate ion exchange
30 materials is disclosed in U.S. Patent 3,985,669. An especially preferred hydrated aluminosilicate has the formula:



wherein x is from about 20 to about 30, especially 28.

35 Other detergency builders include the water-soluble alkali metal (or ammonium) phosphates, polyphosphates, phosphonates, carbonates, silicates, acetates, polyhydroxysulfonates and, especially, polycarboxylates. Various polycarboxylate builders are disclosed in U.S. Patents 3,308,067; 3,723,322; 4,144,226; and 4,246,495. The oxydisuccinates (aka "oxodisuccinates") the

tartrate mono- and di-succinates, and citrate are specific examples of preferred polycarboxylate builders for use herein.

5 The laundry detergent compositions herein can also optionally include clay soil removal and/or antiredeposition agents, and such materials are usually employed in ranges from about 0.1% to about 10% by weight of the compositions. Such materials include various ethoxylated amines, and the like, referred to in the above-cited U.S. Patent 4,711,730. Another group of preferred clay soil removal/antiredeposition agents are the cationic compounds
10 disclosed in European Patent Application 111,965, published June 27, 1984. Such materials are also disclosed in considerable detail in U.S. Patent 4,711,730, cited above.

Other optional ingredients which can be included in laundry detergent compositions of the present invention in their conventional art-established levels for use (i.e., from about 0% to about 20%, by weight) include solvents, bleaching agents, bleach
15 activators, corrosion inhibitors, dyes, fillers, optical brighteners, germicides, pH-adjusting agents, enzymes, enzyme stabilizers, perfumes, and the like. The inclusion of such optional ingredients in fully-formulated detergent compositions is a matter of discretion, according to the objectives of the formulator.
20

Granular detergent compositions embodying the sra's of the present invention can be formed by dry-mixing the sra's into compositions formed by otherwise conventional techniques, conventional
25 techniques, i.e., by slurring the other individual components in water and then atomizing and spray-drying the resulting mixture, or by pan or drum granulation of the ingredients, or by fluidized bed processes.

Liquid formulations can be in the form of single phase (preferred) compositions or can be in multiphase or "dispersion" form. Dispersions conventionally employ viscosity modifiers to produce systems having plastic shear characteristics to maintain stable dispersions and to prevent phase separation or solids
30 settlement.

35 While the laundry detergent compositions of the present invention are operative within a wide range of wash pH's, they are particularly suitable when formulated in liquids to provide a near neutral wash pH, i.e., an initial pH of from about 6.0 to about 8.5 at concentrations of from about 0.1% to about 2% by weight in

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water at 20°C. The near neutral pH of such formulations is also desirable to ensure long-term stability for the sra's. In such formulations, the product pH is preferably from about 6.5 to about 8.5, and more preferably from about 7.0 to about 8.0.

5 The following illustrate specific embodiments of laundry detergent compositions employing the sra's of the present invention, but are not intended to be limiting thereof.

EXAMPLE XII

A liquid detergent composition is as follows.

10	<u>Ingredient</u>	<u>Wt. %</u>
	SRA*	1.0
	Sodium C ₁₂ alkyethoxy (1) sulfate	9.5
	C ₁₂ -C ₁₃ alcohol polyethoxylate	10.2
	C ₁₂ -14 N-methyl glucamide	7.0
15	Ethanol	5.5
	Sodium ethylenediamine tetraacetate	0.3
	Minors and H ₂ O	Balance

*SRA per Example I, above.

EXAMPLE XIII

20 A granular detergent composition is as follows.

	<u>Ingredient</u>	<u>Wt. %</u>
	SRA*	3.5
	C ₁₂ -C ₁₃ alcohol polyethoxylate	20.0
	MgSO ₄	1.0
25	Zeolite 4A hydrate (1-10 micron)	26.0
	Na ₂ CO ₃	18.3
	NaHCO ₃	15.0
	Maxatase MP (protease)	1.5
	Brightener	1.2
30	Water and minors	to 100

*SRA per Example II, above, enrobed in polyethylene glycol avg. m.w. 8,000.

The composition of Example XIII is prepared using standard admix procedures to incorporate the sra.

35 As can be seen from the foregoing, the sra's of the present invention can be employed in laundry and softening compositions of a type familiar to formulators of fabric care compositions. In alternative modes, the sra's herein can be directly added to, for example, aqueous laundry rinse baths in conjunction with fabrics.

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In yet another mode, the sra's herein can be releasably affixed to sheet substrates, or the like, designed for use in automatic clothes dryers. Such sheet substrates can additionally have releasably affixed thereto various fabric softener and/or anti-static agents of types which are well-known in commercial practice. In use, damp fabrics are tumbled with the sheet substrates, thereby causing the sra and, if present, optional fabric softeners/antistatic agents, to be transferred from the sheet substrate onto the fabric surfaces. These and other modes of application of the sra's to fabrics are also contemplated herein.

While the foregoing Examples illustrate the preferred capped sra's, the following illustrates the optional uncapped sra's also encompassed by this invention. It will be appreciated that the uncapped sra's can be used in laundry formulations, as disclosed above.

EXAMPLE XIV

Synthesis of an Uncapped Oligomer of Dimethyl Terephthalate, Poly(Ethylene Glycol) (MW=1450), Ethylene Glycol, and Propylene Glycol (with E/P=2.2) - To a 250 ml, three-neck, round bottom flask equipped with a magnetic stirring bar, modified Claisen head, condenser (set for distillation), thermometer, and temperature controller (THERM-O-WATCH, I²R) is added poly(ethylene glycol) of MW 1450 (Union Carbide, 93.3 g, 0.064 mol), dimethyl terephthalate (25.0 g, 0.129 mol), ethylene glycol (Baker, 16.0 g, 0.258 mol), 1,2-propylene glycol (Fisher, 19.6 g, 0.258 mol), and hydrated monobutyltin oxide (M&T Chemicals, 0.27 g, 0.2% of total reaction weight). This mixture is heated to 180°C and maintained at that temperature overnight under argon as methanol and water distill from the reaction vessel. A ¹³C-NMR(DMSO-d₆) shows this stage of the reaction to be complete by the disappearance of the resonance for methyl esters at -52 ppm. The material is transferred to a 500 ml, single neck, round bottom flask and heated gradually over about 20 minutes to 240°C in a Kugelrohr apparatus (Aldrich) at about 1 mm Hg and maintained there for 40 minutes. The flask is then allowed to air cool quite rapidly to near room temperature under vacuum (~30 minutes). The reaction yields 94.8 g of orange soft solid. A ¹³C-NMR(DMSO-d₆) shows a resonance for -C(O)OCH₂CH₂OC(O)- at -63.2 ppm (diester), a resonance for -C(O)OCH₂CH₂OH at -59.4 ppm (monoester), and a large

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peak at -69.8 representing poly(oxyethylene) units. The ratio of the diester peak height to the monoester peak height is about 5.8. The appreciable concentration of end groups consisting of monoesters of ethylene glycol shows that the product is a low molecular weight polymer. The $^1\text{H-NMR}(\text{DMSO-d}_6)$ spectrum is also consistent with the formation of a low molecular weight polymer. Peaks in the 1.1-1.3 ppm region show an appreciable level of monoesters of propylene glycol are present. The ratio of the area of the peak for the methylene groups of diesters of ethylene glycol at -4.7 ppm to the area of the peak for the methyl group of diesters of propylene glycol at -1.4 ppm is measured. From this, the molar ratio of incorporated ethylene/propylene glycols (E/P ratio) is calculated to be 2.2:1. The solubility is tested by weighing a small amount of material into a vial, adding enough distilled water to make a 5% by weight solution, and agitating the vial vigorously. The material is soluble under these conditions.

As can be seen from the foregoing, a wide variety of fabric softener compositions and laundry detergent compositions can be prepared using the sra's herein. Indeed, modern liquid fabric softeners are currently being provided as high liquid (H_2O) concentrates (5X-6X) which are designed to be diluted with water by the consumer, in-home. Thus, the concentration of ingredients per Example XI, hereinabove, can be essentially doubled to provide such high concentrates. Thus, compositions comprising from about 10% to about 32% by weight of cationic fabric softener (e.g., DTDMAC), from about 4% to about 20% by weight of imidazolinium fabric softener and from about 1% to about 5% by weight of the sra's herein are also encompassed by this invention.

With regard to laundry detergent compositions, highly preferred compositions comprise from about 0.3% to about 3% by weight of the sra's herein and, as the deterative surfactant, from about 3% to about 20% by weight of a fatty acid polyhydroxy amide surfactant (see U.S. Patent 2,965,576, corresponding to GB 809,060, cited above, incorporated herein by reference), preferably in combination with from about 5% to about 25% by weight of a sulfated or sulfonated anionic surfactant such as the C_{12} - C_{18} alkyl benzene sulfonates, C_{12} - C_{18} alkyl ethoxy sulfonates (avg. EO 3-10; preferred), along with conventional amounts (15%-50%) of conventional builders, including such preferred

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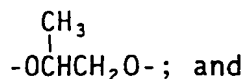
builders as Zeolite A, oxydisuccinates, and mixtures thereof, the balance of such compositions comprising conventional detergent ingredients at conventional levels.

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CLAIMS

1. Soil release agents which comprise the oligomeric esterification product of a reaction mixture which comprises:

- (a) optionally, a source of C₁-C₄ alkoxy-terminated (preferably, methoxy-terminated) polyethoxy units or, optionally, mixtures of said terminated polyethoxy units which incorporate small amounts of propoxy units;
- (b) a source of terephthaloyl units or, optionally, mixtures of terephthaloyl and small amounts of isophthaloyl units;
- (c) a source of poly(oxyethylene)oxy units -(OCH₂CH₂)_y-O-;
- (d) a source of oxyiso-propyleneoxy units



- (e) a source of oxyethyleneoxy units -OCH₂CH₂O-;

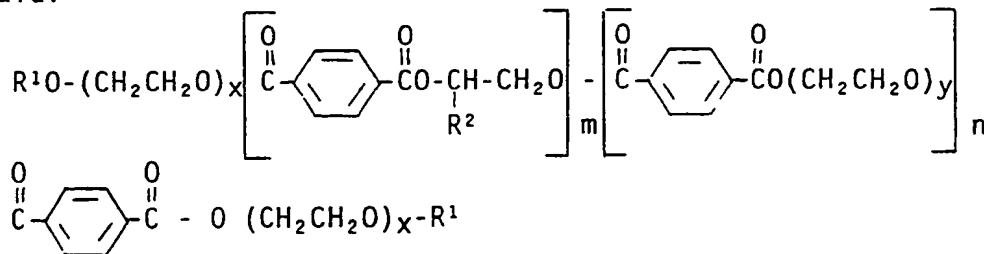
said soil release agents being further characterized by having a mole ratio of oxyethyleneoxy units:oxyiso-propyleneoxy units of at least 0.5:1.

2. A soil release agent according to Claim 1 which comprises the esterification reaction product of a reaction mixture comprising:

- (a) CH₃(OCH₂CH₂)₁₆OH;
- (b) dimethyl terephthalate;
- (c) polyethylene glycol 1500;
- (d) 1,2-propylene glycol; and
- (e) ethylene glycol;

wherein the mole ratio of oxyethyleneoxy units:oxyiso-propyleneoxy units is at least 0.5:1.

3. A soil release agent according to Claim 1 of the general formula:



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wherein R^1 is lower (e.g., C_1 - C_4) alkyl, especially methyl; x and y are each integers from 6 to 100; m is an integer of from 0.75 to 30; n is an integer from 0.25 to 20; and R^2 is a mixture of both H and CH_3 to provide a mole ratio of oxyethyleneoxy:oxyisopropyleneoxy of at least 0.5:1.

4. A soil release agent according to Claim 1 wherein the mole ratio of oxyethyleneoxy:oxyisopropyleneoxy units is at least 0.75:1, preferably 1.25:1.
5. A method for providing a soil release finish on fabrics by contacting said fabrics with an aqueous medium containing at least 2 ppm of the soil release agent of Claim 1.
6. Laundry compositions in the form of detergents, softeners, rinse aids, and the like, comprising at least 0.1% of the soil release agent of Claim 1.
7. A fabric softener composition according to Claim 6 which comprises from 0.3% to 3% by weight of the soil release agent and from 3% to 25% by weight of a fabric softener component.
8. A dilutable liquid fabric softener composition according to Claim 6, comprising:
 - (a) from 10% to 32% by weight of a cationic fabric softener;
 - (b) from 4% to 20% by weight of an imidazolinium fabric softener; and
 - (c) from 1% to 5% by weight of said soil release agent.
9. A laundry detergent composition, comprising conventional deterative surfactants, optional builders, optional carriers, and from 0.1% to 5% by weight of a soil release agent according to Claim 1.
10. A composition according to Claim 9 which comprises from 0.3% to 3% by weight of said soil release agent and from 3% to 20% by weight of a fatty acid polyhydroxy amide surfactant.

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all) ⁶		
According to International Patent Classification (IPC) or to both National Classification and IPC Int.Cl. 5 C08G63/672; C11D3/37		
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁷		
Classification System	Classification Symbols	
Int.Cl. 5	C08G ; C11D	
Documentation Searched other than Minimum Documentation to the extent that such Documents are included in the Fields Searched ⁸		
III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹		
Category ¹⁰	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
X	EP,A,0 241 985 (THE PROCTER & GAMBLE COMPANY) 21 October 1987 see claims 1-4	1,3
A	see claims 1-7 & US,A,4 711 730 8 December 1987 cited in the application ---	1,5-8
X	US,A,4 756 850 (B.C. NAYAR) 12 July 1988 see column 7, line 13 - line 24 ---	1,3
X	EP,A,0 220 156 (THE PROCTER & GAMBLE COMPANY) 29 April 1987 see page 5, line 16 - line 52 ---	1,3
A	EP,A,0 272 033 (THE PROCTER & GAMBLE COMPANY) 22 June 1988 see claims 1-4,6 ---	1,3-4,9
-/-		
<p>¹⁰ Special categories of cited documents :</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"&" document member of the same patent family</p>		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report	
22 JULY 1992	31. 07. 92	
International Searching Authority	Signature of Authorized Officer	
EUROPEAN PATENT OFFICE	K.Y.-P. Miao <i>K.Y.-P. Miao</i>	

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
Category °	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No.
A	GB,A,1 534 641 (UNILEVER LIMITED) 6 December 1978 see claims 1-2 ---	1,9-10

**ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO.**

US 9202256
SA 59391

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.
The members are as contained in the European Patent Office EDP file on
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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A-0241985	21-10-87	US-A- 4711730	08-12-87
		AU-B- 600870	23-08-90
		AU-A- 7150687	22-10-87
		JP-A- 63000312	05-01-88
US-A-4711730	08-12-87	AU-B- 600870	23-08-90
		AU-A- 7150687	22-10-87
		EP-A, B 0241985	21-10-87
		JP-A- 63000312	05-01-88
US-A-4756850	12-07-88	EP-A- 0294886	14-12-88
EP-A-0220156	29-04-87	US-A- 4661267	28-04-87
		AU-B- 582980	13-04-89
		AU-A- 6413786	30-04-87
		CA-A- 1267756	17-04-90
		GB-A, B 2181759	29-04-87
		JP-A- 62161899	17-07-87
EP-A-0272033	22-06-88	AU-A- 8253987	16-06-88
		JP-A- 63253053	20-10-88
GB-A-1534641	06-12-78	None	

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For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

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